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^{141}Pr AND ^{169}Tm NMR STUDY OF SUPERCONDUCTING PrCeCuO AND TmBaCuO

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The NMR spectra and nuclear relaxation of $^{141}Pr^{3+}$ and $^{169}Tm^{3+}$ ions in oriented powders of high-T_c superconductors $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (T_c=24K) and $TmBa_2Cu_3O_{7-y}$ (T_c=91K) at temperatures well below T_c were investigated. The relaxation of Pr nuclear transverse magnetization at temperatures down to 0.05K gives an evidence for the trivalent state of Ce ions in the superconducting phase of the PrCeCuO compound. Two types of Tm centers in TmBaCuO were observed (of orthorhombic and tetragonal symmetry), exhibiting similar parameters of NMR spectra, but completely different relaxation rates. Anomalously slow nuclear transverse relaxation of tetragonal Tm centers at liquid helium temperatures allows one to conclude that those centers are formed by single Tm ions and/or small clusters.

Many of high-T_c superconductors contain rare-earth (RE) ions with an even number of 4f-electrons, such as Pr^{3+}, Tb^{3+}, Ho^{3+}, Tm^{3+}. The magnetic resonanse of RE nuclei can be observed[1-3] at low temperatures in those substances (called "Van Vleck paramagnets") where the ground state of RE ions in a crystal electric field (CEF) is a singlet, whereas the excited 4f-states are separated from the ground one by energies of 10-100cm^{-1}. First NMR experiments on ^{141}Pr (I=5/2) and ^{169}Tm (I=1/2) nuclei in oriented ceramic powders of Van Vleck (VV) paramagnets $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ and $TmBa_2Cu_3O_{7-y}$ ($y\approx0.1$) clearly demonstrate the efficiency of the RE NMR studies for obtaining new information on high-T_c superconductors. Both compounds under study are known[4,5] to have the lowest excited CEF 4f-states at energies ~100cm^{-1}.

The samples were prepared following standard ceramic procedures. Both samples were single phase to 5% as determined by X-ray diffraction. The powders were oriented in a field of 15kOe by using a rotating container with molten paraffin (PrCeCuO) and sulphur (TmBaCuO). A conventional home-built coherent-pulse NMR spectrometer with $\pi/2-\tau-\pi$ pulse sequence was used both for spectral and relaxation measurements. The temperatures down to 0.05K were obtained by using the ^3He-^4He dilution refrigerator.

The non-superconducting metallic praseodimium VV paramagnets are known to be unsuitable samples for pulsed NMR experiments because of the extremely short relaxation times of Pr nuclei[1,6]. Therefore, we believe that all Pr NMR spectra, which were observed in $Pr_{1.85}Ce_{0.15}CuO_{4-y}$[7,8] (for example see Fig.1), must be assigned to the superconducting (SC) phase. The spectra can be described by the spin-Hamiltonian of an axial symmetry[1], its parameters being in a satisfactory

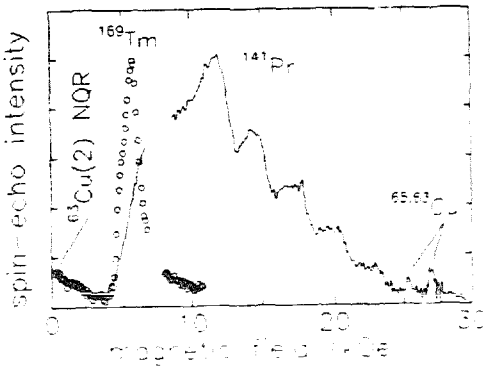

Fig. 1. NMR spectra of Tm nuclei in TmBaCuO (open circles-T=1.5K, θ=90°, τ=15μs) and Pr nuclei in PrCeCuO (solid line-T=2.4K, θ=0°, τ=6μs) at the frequency of 30.5MHz. θ is the angle between the applied field $\vec{H}$ and the c'-direction of the predominant orientation of crystallites c-axes.

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